VIBRATIONAL SPECTROSCOPY AT THE SERVICE OF QUANTUM CHEMISTRY

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Vibrational spectroscopists profit enormously from the advances in quantum chemistry codes for spectral assignment and interpretation. This is certainly true for the study of weakly bound complexes, often generated in supersonic jet expansions with limited equilibration. It is time to pay back for this valuable support by generating dedicated new experimental data which can help theory to assess the quality of their approximate methods. This is complementary and in the end perhaps superior to important theory-internal benchmarking activities, which rely on a hierarchy of methods and may be limited in molecular complexity [1]. Experimental benchmarking only works if every effort has been made to secure the results. It comes in two variants, which can alternate with each other, to systematically approach the right answers for the right reasons. Blind challenges hide the experimental result and invite theory groups to predict it [2], followed by full disclosure and a discussion of the theory performance. Databases provide carefully curated compilations of spectroscopic observables [3], to save the interested theoreticians from tedious searches and misinterpretation. The talk will address a few examples from the Göttingen research training group BENCh [4], to convey the general idea. Close competition between conformational energies or for spectral properties are particularly valuable, because they invite binary decisions [5]. If you got a nice spectroscopy experiment running in your lab, choose and publish your systems and observable quantities in a way which is useful and challenging for the benchmarking of computational methods! If your experiment is reasonably unique but still well tested against others, consider to organize a blind challenge! If you are a theoretician, try to put your models to the (blind) test by experiment, although it seems so much easier to compare them to a reference theory!

[1] R. A. Mata, M. A. Suhm: Angew. Chem. Int. Ed. 56 (2017) 11011–11018 [2] T. L. Fischer, M. Bödecker, A. Zehnacker-Rentien, R. A. Mata, M. A. Suhm: Phys. Chem. Chem. Phys. 24 (2022) 11442–11454 [3] Challenges for Numerical Quantum Chemistry: https://qmbench.net/ [4] Benchmark Experiments for Numerical Quantum Chemistry: https://uni-goettingen.de/en/587836.html [5] R. Medel, J. R. Springborn, D. L. Crittenden, M. A. Suhm: Molecules 27 (2022) 101